

## PATENT SPECIFICATION

NO DRAWINGS

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International Classification:—C 07 f (C 08 f, g).

## COMPLETE SPECIFICATION

## Hydroxy Alkoxy Alkyl Phosphites

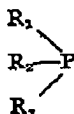
We, PURE CHEMICALS LIMITED, a British Company, of Stockpit Road, Kirkby Industrial Estate, Liverpool, Lancashire England, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed to be particularly described in and by the following statement:—

This invention relates to tertiary phosphite esters of polypropylene glycols.

It is an object of the present invention to prepare novel phosphites.

Another object is to prepare linear monomeric tertiary phosphites from polyhydric alcohol.

It has now been found that these objects can be attained by preparing tertiary phosphites having the formula



where  $R_1$  is  $\text{HOCH}_2\text{CH}_2(\text{OCH}_2\text{CH}_2)_x\text{O}$



and  $x$  is an integer of at least 1 and  $R_2$  and  $R_3$  are the same as  $R_1$  or are aryloxy or alkoxy. Preferably  $R_2$  and  $R_3$  are the same as  $R_1$ , i.e., all of them are polypropylene glycol residues. While  $R_1$  grouping is written as  $\text{HOCH}_2\text{CH}_2(\text{OCH}_2\text{CH}_2)_x\text{O}$  since the vast

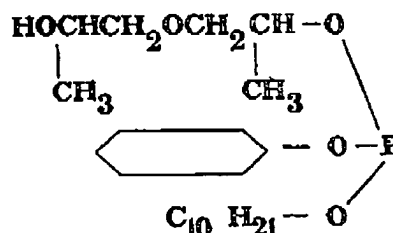
majority of the groupings present (e.g. about 90%) will have this secondary alcohol relationship, still there will be some units in the product having the  $\text{HOCH}_2\text{CH}_2(\text{OCH}_2\text{CH}_2)_x\text{O}$

grouping and other units will have the

$\text{HOCH}_2\text{CH}(\text{OCH}_2\text{CH}_2)_x\text{O}$  grouping.



Examples of polypropylene glycol phosphites within the present invention are tris-dipropylene glycol phosphite, tris-polypropylene glycol 425 phosphite, tris-polypropylene glycol 1025 phosphite, tris-polypropylene glycol 2025 phosphite, tris-polypropylene glycol 3000 phosphite, bis-dipropylene glycol phenyl phosphite, bis-dipropylene glycol decyl phosphite, bis-dipropylene glycol p-cresyl phosphite, bis-dipropylene glycol octadecyl phosphite, bis-polypropylene glycol 425 phenyl phosphite, bis-polypropylene glycol 425 decyl phosphite, bis-polypropylene glycol 1025 octadecyl phosphite, dipropylene glycol bis-phenyl phosphite, dipropylene glycol bis-decyl phosphite, dipropylene glycol bis-octadecyl phosphite, dipropylene glycol bis o-cresyl phosphite, polypropylene glycol 425 bis-phenyl phosphite, polypropylene glycol 1025 bis-decyl phosphite, dipropylene glycol phenyl decyl phosphite.



The new phosphite esters have many uses. Thus, they are stabilizers for polyether polyurethanes against oxidation and degradation (as demonstrated in retarding the yellow or brown color common to such urethanes which

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have been exposed to air or light) and serve as plasticizers for polyurethanes, and the like.

The tris-polypropylene glycol phosphites are particularly useful. Because of their hydroxyl functionality they are excellent for incorporation into urethane systems where they react with the isocyanate end groups in the growing polymer chain and thus become fixed. Due to their poly functionality they serve to also crosslink and strengthen the polymer chain.

The tris-polypropylene glycol phosphites can also be incorporated into epoxy resin systems. Thus, tris-dipropylene glycol phosphite can react directly in an epoxy system catalyzed preferably by an alkyl amine. The tris-polypropylene glycol phosphite can be prereacted with maleic anhydride or other polybasic acid or anhydride to give the corresponding acid ester phosphite ester which can react in many epoxy systems without additional catalyst.

The tris-polypropylene glycol phosphites also can be employed to form polyesters, e.g., by reaction, e.g. mole for mole with maleic anhydride, phthalic anhydride, dimethyl terephthalate, fumaric acid, succinic acid, oxalic acid, itaconic acid.

The novel phosphites are also useful as lubricants, heat transfer fluids, hydraulic fluids and pump fluids. They have good fluid properties, are insoluble in water and have in effect a built-in stabilizer and acid acceptor. They are also suitable as plasticizers in polyester systems and free radical formed systems, e.g., polymerized methyl methacrylate. They can be used in existing glycol type lubricants and fluids.

The polypropylene glycol phosphites are prepared by transesterifying a triaryl phosphite or a trialkyl phosphite with a polypropylene glycol. To prepare a tris polypropylene glycol phosphite at least 3 moles of polypropylene glycol should be employed per mole of triaryl or trialkyl phosphite. Preferably a slight excess of the polypropylene glycol is employed. To prepare bis polypropylene glycol mono aryl or mono alkyl phosphites only two moles of polypropylene glycol are employed per mole of triaryl or trialkyl phosphite. To prepare mono polypropylene glycol bis aryl or bis alkyl phosphites only one mole of polypropylene glycol is employed per mole of triaryl or trialkyl phosphite. When less than three moles of polypropylene glycol are employed per mole of triaryl or trialkyl phosphite there is some tendency for polymer formation as a by-product. Such by-products can be used in the same manner as the monomeric products.

As the polypropylene glycol there can be employed dipropylene glycol, polypropylene glycol 425 (polypropylene glycol having an average molecular weight of 425), polypropylene glycol 1025 (polypropylene glycol having an average molecular weight of 1025), poly-

propylene glycol 2025 (polypropylene glycol having an average molecular weight of 2025) and polypropylene glycol having an average molecular weight of 3000 or mixtures thereof.

As the triaryl or trialkyl phosphite there can be used for example triphenyl phosphite tri-o-cresyl phosphite, tri-p-cresyl phosphite, tri-m-cresyl phosphite, tri-xylene phosphite, tri-decyl phosphite, diphenyl decyl phosphite, and tri-ethyl phosphite.

The reaction can be catalyzed by alkaline catalysts, e.g., 0.1—10% of sodium phenolate, sodium cresylate, potassium phenolate, sodium methyllate, sodium decylate, sodium dipropylene glycolate or the like, or can be catalyzed with a diaryl or dialkyl phosphite, e.g., 0.1—1% of diphenyl phosphite, di-o-cresyl phosphite, di-p-cresyl phosphite, dimethyl phosphite, diethyl phosphite didecyl phosphite, dioctadecyl phosphite.

When alkaline catalysts are employed preferably they have a pH of at least 11 in a 0.1 N solution.

Due to the fact that the alcohol groups in dipropylene glycol (and the other polypropylene glycols) are secondary and hence relatively slow in reacting, it is possible to prepare the tris polypropylene glycols having three functional hydroxyl groups with a minimum of cross-linking or polymerization. The tris polypropylene glycol products are insoluble and not subject to hydrolytic attack by water.

The higher polypropylene glycol phosphites can be prepared by reacting tris dipropylene glycol phosphite with propylene oxide. Reaction occurs at the free hydroxy sites and a tris polypropylene glycol phosphite results.

Unless otherwise indicated, all parts and percentages are by weight.

#### EXAMPLE 1.

Triphenyl phosphite 3100 grams (10 moles), diphenyl phosphite 15 grams (catalyst) and di-propylene glycol 4422 grams (33 moles, a 10% excess) were heated in vacuo (10 mm.) at 120°C. Phenol was collected (bp. 85—90°C. 10 mm.). As the reaction proceeded the pot temperature was allowed to rise to 155°±5°C. During this time, the distillate consisted of pure phenol until about 80% of the theoretical amount was collected.

Thereafter, it was contaminated with increasing amounts of dipropylene glycol. The reaction was completed when 3250 grams of combined distillate was obtained. The pot residue after filtration through Filtercel (Registered Trade Mark) (diatomaceous earth) was tris dipropylene glycol phosphite, a viscous colorless liquid and had an  $n_D^{25}$  1.4610,  $d_4^{25}$  1.097.

#### EXAMPLE 2.

In the same manner as Example 1 there were reacted triphenyl phosphite 3100 grams

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(10 moles), diphenyl phosphite 15 grams (catalyst) and polypropylene glycol 425 in an amount of 12750 grams (30.3 moles). Heating was continued until 2780 grams of phenol (97% of theory) were recovered. The tris polypropylene glycol 425 phosphite left in the pot was a colorless viscous liquid and had an  $n_D^{25}$  1.4535 and a  $D_4^{25}$  1.028.

## EXAMPLE 3.

Polypropylene glycol 1025 (9235 grams, 9.09 moles), triphenyl phosphite (930 grams, 3 moles) and diphenyl phosphite (20 grams, catalyst), were heated together in vacuo with stirring to a temperature of 210°C. and 5 mm. pressure. Phenol, m.p. 40°C. was collected (816 grams). The mixture was then swept with nitrogen for 2 hours at 210–220°C. 10 mm. pressure to complete the phenol distillation. An additional 34 grams was collected. Total yield of phenol, 850 grams (846 grams theoretical ÷ 18 grams from catalyst or a total of 864). The pot residue was allowed to cool to 150°C. treated with clay and filtered to give tris-polypropylene glycol 1025 phosphite in almost theoretical yield a liquid having the following properties:  $n_D^{25}$  1.4515 Sp. G.<sub>25</sub> 1.022.

## EXAMPLE 4.

In a similar manner polypropylene glycol 2025 (18,216 grams, 9.09 moles), triphenyl phosphite (930 grams, 3 moles) and diphenyl phosphite (50 grams catalyst) were reacted to give tris-polypropylene glycol 2025 phosphite in almost theoretical yield as a liquid having the properties:  $n_D^{25}$  1.4501 Sp. G.<sub>25</sub> 1.006.

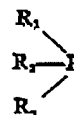
## EXAMPLE 5.

Dipropylene glycol (884 grams, 616 moles) 10% excess, triphenyl phosphite (610 grams, 2 moles) and sodium (0.5 g dissolved in a little dipropylene glycol) was reacted as described in Example 1. About 90% of the phenol was distilled out from the reaction mixture free of co-distilled dipropylene glycol. Towards the end of the reaction of a mixture of phenol and glycol was obtained. The pot residue after treatment with clay and subsequent filtration was identical in every respect to material prepared as per example 1.

Alkaline catalysts can also be employed with high polypropylene glycol to make the phosphite esters.

## WHAT WE CLAIM IS:—

1. A process of preparing a polypropylene glycol phosphite comprising heating at least one mole of a polypropylene glycol with one mole of a triaryl phosphite or a trialkyl phosphite. 55
2. A process of preparing a tris polypropylene glycol phosphite comprising heating at least 3 moles of polypropylene glycol with one mole of a triaryl or trialkyl phosphite in the presence of a diaryl or dialkyl phosphite as a catalyst or an alkaline catalyst. 60
3. A process of preparing a bis polypropylene glycol monoaryl or monoalkyl phosphite comprising heating two moles of polypropylene glycol with one of a triaryl or trialkyl phosphite in the presence of a diaryl or dialkyl phosphite or an alkaline catalyst. 65
4. A process of preparing a monopropylene glycol diaryl or dialkyl phosphite comprising heating one mole of polypropylene glycol with one mole of triaryl or trialkyl phosphite, in the presence of a diaryl or dialkyl phosphite or an alkaline catalyst. 70
5. A process according to claim 2, 3 or 4 wherein the alkaline catalyst is a metal alcoholate or a metal phenolate. 75
6. A compound of the formula 80



where  $R_1$  is a polypropylene glycol residue having predominantly the structure  $HOCHCH_2(OCH_2CH_2)_XO$  and X is an integer

of at least one and  $R_2$  and  $R_3$  are selected from  $R_1$ , alkoxy and aryloxy. 85

7. Tris polypropylene glycol phosphites. 85
8. Tris dipropylene glycol phosphite.
9. Tris polypropylene glycol 425 phosphite. 90
10. Tris polypropylene glycol 1025 phosphite.
11. Tris polypropylene glycol 2025 phosphite.

MARKS & CLERK,  
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